The Oceans & Carbonate Chemistry

Summary

Grade Level: 10 - 12 **Teaching Time: 40 minutes Activities:**

- Use an online simulation to examine the effects of changing atmospheric CO₂ and temperature on sea water pH and carbonate concentrations over time.
- Apply simulation to different model-based scenarios of future CO₂ levels.

Objective

Students will use online tools to recreate climate change model scenarios and examine effects of increased CO₂ on ocean acidity and carbonate saturation levels.

Background

One reason models are useful is that they allow scientists to use what they know of the past and present to project possible future conditions. If the processes dependent on model parameters continue to work in the same way as they do now, what effects will changing those model parameters have in the future? For example, what would the effects be on ocean pH and on coral reefs if atmospheric CO₂ levels continue to rise?

Scientists worldwide have worked on many different models, attempting to use various types of current and historical data to predict future changes in atmospheric CO₂, global temperature, sea-level increases, etc. Much of this work has been gathered in one place by the International Panel on Climate Change (IPCC). One result of the IPCC's work is the creation of several possible future scenarios for the changing amounts of atmospheric CO₂ over time and the predicted consequences.

Vocabulary

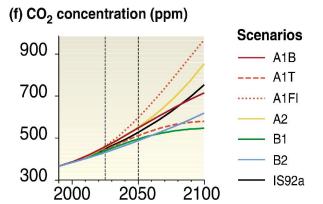
bicarbonate – an ion HCO₃ formed when carbonic acid (H₂CO₃) loses an H⁺ ion. A bicarbonate ion has a charge of negative one.

carbonate – an ion CO₃ formed when bicarbonate (HCO₃) loses an H⁺ ion. A carbonate ion has a charge of negative two.

aragonite – a mineral form of calcium carbonate CaCO₃ that is often used by marine life to form skeletons and shells.

simulation – a model that attempts to recreate how a real system or environment works.

pCO₂atm – the partial pressure of carbon dioxide in the atmosphere.



Source: **IPCC, 2001:** Climate Change 2001: Synthesis Report. A Contribution of Working Groups I, II, and III to the Third Assessment Report of theIntegovernmental Panel on Climate Change [Watson, R.T. and the Core Writing Team (eds.)]. Cambridge University Press, Cambridge,United Kingdom, and New York, NY, USA, 398 pp.

In the A1 scenarios, the IPCC model projects rapid worldwide economic growth. Population peaks mid-century. The A1Fi is the "worst case" scenario in which energy continues to be mainly derived from burning fossil fuels. A1T imagines energy as having moved to non-fossil fuels. A1B splits the difference between fossil and non-fossil fuels based scenarios.

The B scenarios imagine a somewhat rosier picture. In the B scenarios, world population still peaks mid-century. And, while these B scenarios see world and regional economies growing, they see that the types of economies move away from an emphasis on heavy industry and toward service and information economies. Emphasis is placed on cleaner, more efficient technologies.

Preparation

Familiarize yourself with the online carbonate simulation, so that you can demonstrate it to your class using a computer and projector. The purpose of the interactive carbonate simulation is to help students see the generalized effects of rising atmospheric CO₂ and changing water temperature on ocean pH and carbonate levels necessary for reef development.

Vocabulary

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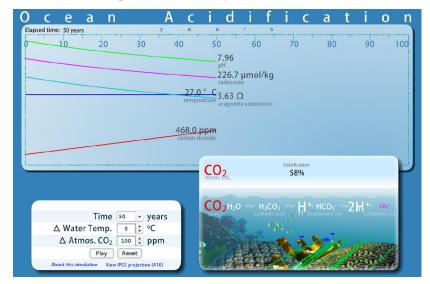
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- Visit <u>www.dataintheclassroom.org</u> and click on the Ocean Acidification module link.
- 2. Follow the link to "Carbonate Simulation."
- 3. In this activity, students will be using the simulation to investigate how increased CO₂ in the atmosphere affects pH and the carbonate buffering system reactions in seawater. The available inputs are time (in years), change in ocean surface water temperature (in degrees C), and change in atmospheric CO₂ (in ppm). Note that the changes occur over the period of time chosen. An increase of 100 ppm CO₂ over 10 years (10 ppm/year) is significantly greater than an increase of 100 ppm CO₂ over 100 years (1 ppm/year). Also note that the atmospheric CO₂ assumes a base value of 368 ppm. Changes in atmospheric CO₂ are increases above that 368 ppm baseline, which was the level of atmospheric CO₂ in the year 2000.



- 4. Change the "Time" setting to 50 years.
- 5. Change the "Δ Water Temp." setting to 0.5 °C. For the purposes of the simulation, water temperature has been separated from the CO₂ input. Therefore, you will not see the water temperature change as a result of changing the CO₂ levels. You may choose to change surface water temperature with the input, either in a

Carbonate Buffer Model

The graphs and data seen in the simulation students use in this activity are based on the CO2SYS program, developed by researchers at the **Brookhaven National** Laboratory. CO2SYS performs calculations relating parameters of the carbon dioxide (CO₂) system in seawater. Using known formulas, the program uses two of the four measurable parameters of the CO₂ system (total alkalinity, total inorganic CO₂, pH, and partial pressure of CO₂) to calculate the other two parameters, plus calcite and aragonite saturation levels, at a set of input and output conditions (temperature and pressure) chosen by the user.

positive or negative direction. However, in an atmosphere with increased levels of CO₂, air temperature will increase over time (greenhouse effect, global warming), resulting in increased ocean surface water temperature. Average annual surface water temperature in the Caribbean Sea is expected to increase by 1.0 to 1.5 degrees Celsius by the end of this century.

- Change the "Δ Atmos. CO₂" setting to 100 ppm. This will
 increase CO₂ by 100 ppm over 50 years. This is equal to the
 current 2 ppm per year increase in atmospheric CO₂ observed by
 researchers.
- 7. Click the Play button to start the simulation. The simulation graph area shows the increasing atmospheric CO₂ accompanied by decreasing ocean pH (i.e., increased ocean acidity) and decreasing levels of carbonates.
- 8. Click the Reset button. Reenter your input choices to repeat the same simulation. This time, when you click Play, watch what happens in the inset window at the lower right of the simulation. The animated coral growth will be affected by the water conditions (i.e., pH, available calcium carbonate). In conditions that are bad for coral growth, the calcification rate will decrease, sea grass will increase, and fish populations decrease. The carbonate buffering system equations are also animated, with components increasing or decreasing in size to reflect what happens over time.

Materials

- Computer or overhead projector
- Copies of Student Master
- Student access to computers with Internet connection

Procedure

This activity uses guided inquiry to accomplish two objectives: 1) for students to become familiar with the complex carbonate buffering system present in Earth's oceans; and 2) for students to understand the implications of increased atmospheric CO₂ on the ocean carbonate system, ocean acidity, and the ability of marine organisms to create their skeletons.

1. First show students the Teacher Master and go through the chain of chemical equations that make up the carbonate buffer system. Students may already be familiar with the first few steps if they have done Level 2 of the Ocean Acidification module. In the first chemical equation, carbon dioxide from Earth's atmosphere enters the ocean at the air/water contact and reacts with water to form carbonic acid:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

The carbonic acid almost immediately dissociates in water, releasing the hydrogen and bicarbonate ions:

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

The bicarbonate ions also dissociate, releasing additional hydrogen ions and forming carbonate ions:

$$H^+ + HCO_3^- \leftrightarrow 2 H^+ + CO_3^{2-}$$

Marine organisms that build calcareous shells use calcium carbonate in the form of the minerals, calcite or aragonite. That calcium carbonate is formed when some of the free bicarbonate ions react with calcium ions in the water to form calcium bicarbonate, which then is used to form calcium carbonate, with carbonic acid (dissociating to bicarbonate and hydrogen ions) as a byproduct:

$$Ca^{2+} + 2HCO_3^- \rightarrow Ca(HCO_3)_2$$

 $Ca(HCO_3)_2 \rightarrow CaCO_3 + HCO_3 + H^+$

These equations make up the carbonate buffer system. In chemistry, a buffer is an ionic compound that resists changes in its pH. Discuss these questions with your students: What is the significance of the equilibrium arrows in the carbonate equations? In what way do carbonate ions buffer the seawater against changes in pH? Students should understand that the reactions in the carbonate buffer system work in both directions. Bicarbonate ions can dissociate to form carbonate and hydrogen ions; that increases hydrogen ion concentration. Going in the other direction, hydrogen ions can combine with carbonate ions to form bicarbonate; this decreases free hydrogen ions, thus buffering the solution by making it more alkaline.

- 3. Use a computer and projector to display the carbonate simulation found online at www.dataintheclassroom.org. Explain the inputs available. Set up the simulation with the inputs you used earlier (time 50 years, Δ Water temp. 0.5 °C, Δ Atmos. CO₂ 100 ppm) and click Play. Have students explain what they observe as outputs in the simulation window. Call attention to units:
 - Changes in CO₂ levels, both input and output, are reported as ppm (parts per million) CO₂.
 - Dissolved carbonate is reported as µmol/kg, which is understood to mean micro-moles of carbonate dissolved in each kg of seawater.
 - Aragonite is reported as Ω , which is the solubility ratio relating actual product of carbonate and calcium to the ideal product. An aragonite Ω value greater than 1 means the seawater is oversaturated with ions necessary to form the mineral aragonite. An aragonite Ω value less than 1 means the seawater is undersaturated with ions necessary to form aragonite.

Focus attention on trends in the lines. Which values go up and which go down? Click Reset and then run the simulation again. This time, have students observe the carbonate equation animation and the coral reef animation in the lower right area of the screen. What happens in each?

4. Give each student a copy of the Student Master, CO₂ and Carbonate Saturation. Students will then follow instructions on the Student Master to gather data online using the carbonate simulation and to answer a set of questions.

Answers:

- 1. The simulation shows minimal effect of increased seawater temperature on pH, and on carbonate and aragonite concentration. Increasing levels of CO₂ in the atmosphere leads to decreased pH (increased ocean acidity), decreased concentrations of carbonate ions, and decreased aragonite saturation levels.
- 2. For high \triangle CO₂, the size of ions changes over time to indicate relative abundance. As time goes on, the concentration of H+ ions increases (which decreases measured pH) and the concentration of carbonate ion decreases.
- 3. No, the pH of seawater never reaches the critical level of 7.66 in any of these three IPCC scenarios.
- 4. Calcification decreases with increased CO₂ levels. In the B2 scenario, calcification efficiency falls from 67 to 45 percent over 100 years. Carbonate and aragonite levels also decrease as CO₂ levels increase.

Carbonate Buffering Equations

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2 H^+ + CO_3^{2-}$$

carbon dioxide water

carbonic acid

hydrogen ion bicarbonate ion

hydrogen ions carbonate ion

$$Ca^{2+} + 2HCO_3^- \rightarrow Ca(HCO_3)_2$$

bicarbonate ions Calcium ion

calcium bicarbonate

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + HCO_3 + H^+$$

calcium bicarbonate

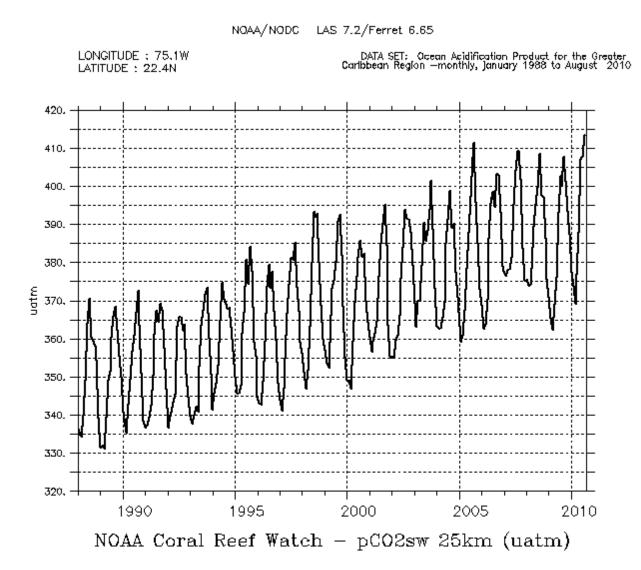
calcium carbonate bicarbonate ion hydrogen ion

Student Master

CO₂ and Carbonate Saturation

If the IPCC best-case scenario for atmospheric CO₂ comes true over the next 100 years, what are the implications for ocean acidity and coral reef development?

The pCO₂sw graph below shows that surface ocean waters in the Caribbean study area have experienced increased concentrations of dissolved CO₂ over the last 15 to 20 years. If atmospheric CO₂ continues to rise, what effect might that have on water pH and on the concentration of dissolved materials needed by marine life to form skeletons?



In this activity, you will use the online carbonate simulation to investigate the impact of changes in dissolved CO₂ and water temperature on pH and carbonate concentrations over time.

- 1. Visit <u>www.dataintheclassroom.org</u> and click on the Ocean Acidification module link.
- 2. Follow the link to "Carbonate Simulation."
- 3. This simulation is set up with inputs for time in years, change in surface water temperature, and change in CO₂ concentration just above the air/water contact. Set the time to 100 years and leave the other two inputs set to their default "0" values. Click Play. You should see that, if the CO2 level remains at the default 368 ppm level, pH and dissolved carbonates (carbonate and aragonite) remain stable. The graphs "flat line."
- 4. Let us see if water temperature has an effect. Select 50 years for "Time."
- 5. To isolate the variables, pick a number for ΔCO_2 and leave that constant while you vary the change in water temperature. For now, use "50" for the "Δ CO₂" input.
- 6. Now try different "Δ Temp" settings and run the simulation. Record the observed data in the table below.

Inputs			Outputs					
Time (years)	Δ Temp (°C)	ΔCO_2 (ppm)	Final water temp (°C)	Final CO ₂ (ppm)	pН	Carbonate (µmol/kg)	Aragonite (Ω)	
50	-1.0	50						
50	0.0	50						
50	+ 0.5	50						
50	+ 1.0	50						
50	+ 2.0	50						

7. Now repeat the process, except this time hold the " Δ Temp" constant at + 0.5 °C and vary the " Δ CO₂" value. After each trial, click Reset and run the simulation a second time with the same settings. Watch the animated coral and animated chemical equations in the lower right window. Record the observed "Calcification" value in the table. The calcification rate displayed in this simulation is an approximation of the corals' calcification efficiency based on 100% efficiency in the year 1880, which was the beginning of the Industrial Era. A calcification rate of 67% means that an organism is only 67% as efficient at precipitating aragonite at that time as it was in 1880 when atmospheric CO₂ levels were much lower.

Inputs			Outputs						
Time (years)	Δ Temp (°C)	Δ CO ₂ (ppm)	Final CO ₂ (ppm)	pН	Carbonate (µmol/kg)	Aragonite (Ω)	Calcification		
50	+ 0.5								
50	+ 0.5								
50	+ 0.5								
50	+ 0.5								
50	+ 0.5								

8. Finally, try approximating three of the IPCC model-based scenarios for CO₂ change in Earth's atmosphere. First look at the A1B "middle of the road" scenario. Click on the "View IPCC projection (A1B)" link at the bottom of the simulation to set the inputs. Click Play. Fill in your observations in the table below.

	Inputs			Outputs					
IPCC Scenario	Time (years)	Δ Temp (°C)	ΔCO ₂ (ppm)	Final CO ₂ (ppm)	рН	Carbonate (µmol/kg)	Aragonite (Ω)	Calcificat ion	
A1B	100	1.3	320						
B2	100	1.0	260						
A2	100	1.5	480						

- 9. Now run the B2 "environment" driven scenario. Use the input values in the table and click Play. Record your observations in the table.
- 10. Finally, run the A2 "economics" driven scenario and record your observations. Our simulator cannot show the effects of the "worst case" IPCC scenario (A1F1). In that "economic" scenario, our simulation would need to have an input of just over 553 ppm for ΔCO_2 .

Questions

- 1. Which has a greater effect on pH, change in temperature or change in CO₂? Which has a greater effect on carbonate and aragonite concentration?
- 2. In the simulation, you observed the carbonate equation as the concentrations of ions changed over time. Describe the changes in the equation over time in trials run with high Δ ppm CO₂.
- 3. Below a pH of 7.40 to 7.66, coral organism are unable to build their skeletons quickly enough to maintain a coral reef. Look at your data table. In any of these three scenarios, does the pH of seawater reach this pH level in 100 years?
- 4. Describe what you observed about calcification in the three scenarios. What other values decrease as CO₂ levels increase?